

# Pd<sup>II</sup>-mediated Integration of Isocyanides and Azide Ion Might Proceed via Formal 1,3-Dipolar Cycloaddition between RNCs Ligands and Uncomplexed Azide

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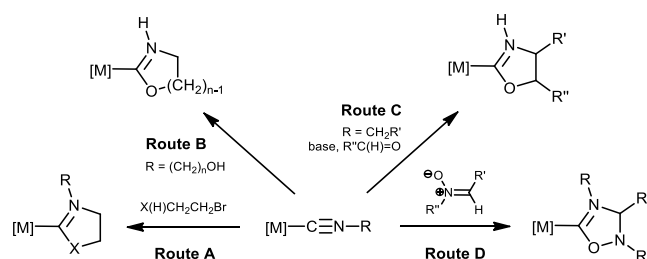
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Reaction between equimolar amounts of *trans*-[PdCl(PPh<sub>3</sub>)<sub>2</sub>(CNR)][BF<sub>4</sub>] (R = *t*-Bu **1**, Xyl **2**) and diisopropylammonium azide **3** gives the tetrazolate *trans*-[PdCl(PPh<sub>3</sub>)<sub>2</sub>(CN<sub>4</sub>*t*-Bu)] (67%, **4**) or *trans*-[PdCl(PPh<sub>3</sub>)<sub>2</sub>(CN<sub>4</sub>Xyl)] (72%, **5**). Complexes **4** and **5** were characterized by elemental analyses (C, H, N), HRESI<sup>+</sup>-MS, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies. In addition, the structure of **4** was elucidated by a single-crystal X-ray diffraction. DFT calculations showed that the mechanism for the formal CA of N<sub>3</sub><sup>−</sup> to *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(CNMe)]<sup>+</sup> is stepwise. The process is both kinetically and thermodynamically favorable and occurs via the formation of the acyclic NNNCN-intermediate. The second step of formal CA, *i.e.* cyclization, is the rate limiting. Despite the fact that the substitution of CNMe by N<sub>3</sub><sup>−</sup> ligand is slightly thermodynamically favorable, we were unable to find paths on the potential energy surface for hypothetical CA between uncomplexed isocyanide and palladium-bound azide. Thus, we believe that the experimentally observed palladium tetrazolate complexes are, in fact, generated from the negatively charged uncomplexed azide and the positively charged metal-bound isocyanide species, and this reaction path is favorable from the viewpoint of Coulomb attraction.

## Introduction

Being one of the most studied ligands in contemporary organometallic chemistry and catalysis, N-heterocyclic carbenes (NHCs) continue to attract a lot of attention due to their valuable characteristics, *e.g.*, high chemical and thermal stability, low toxicity, and variability of donor and steric properties.<sup>1–5</sup> Preparation of metal complexes with NHCs ligands can be achieved via either direct coordination of pre-prepared (or generated *in situ*) free NHCs to metal center,<sup>1–5</sup> or through diverse cyclizations of metal-bound isocyanides and this subject was repeatedly reviewed including recent surveys by some of us.<sup>6–9</sup>

Firstly (**Scheme 1, route A**), cyclic carbenes are prepared via two-step cascade synthesis that includes a nucleophilic attack of an amino or alcohol function of X(H)CH<sub>2</sub>CH<sub>2</sub>Br (XH = OH, NH<sub>2</sub>) on a coordinated isocyanide followed by ring closure.<sup>7,9</sup>



**Scheme 1.** Conversion of ligated isocyanides into *N*-heterocyclic carbene complexes.

Secondly (**route B**), metal-NHCs are generated via a spontaneous or base-promoted intramolecular cyclization of complexes featuring functionalized isocyanides, *e.g.* M–C≡N–(CH<sub>2</sub>)<sub>n</sub>–OH.<sup>9</sup> Thirdly (**route C**), isocyanides bearing acidic C–H bonds in the  $\alpha$ -position to the C≡N group, *e.g.* M–C≡N–CH<sub>2</sub>EWG (where EWG stands for an electron withdrawing moiety), being ionized with a base, react with polar double bonds (*e.g.* with RC(H)=O as a 1,3-dipolarophile) furnishing heterocycles.<sup>10,11</sup>

Finally, complexes with NHC ligands can be generated via a metal-mediated 1,3-dipolar cycloaddition (CA) of some dipoles to isocyanides (**route D**). Examples of the latter route are so far limited to CA of nitrile imines [accomplishing the carbene {C(NR''N=C<sup>a</sup>R')=N<sup>b</sup>R(C<sup>a</sup>–N<sup>b</sup>)}],<sup>12</sup> nitrile ylides<sup>12</sup> [yielding the {C(CHR''N=C<sup>a</sup>R')=N<sup>b</sup>R(C<sup>a</sup>–N<sup>b</sup>)} functionality] and, as we previously

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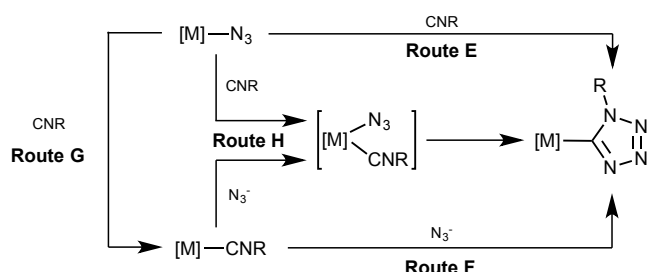
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observed, acyclic and cyclic nitrones [giving the  $\{C(CHR''N=C^aR')=N^bR(C^o-N^b)\}$  moiety] to coordinated RNCs,<sup>13</sup> and the metal-mediated interplay between RNC and azide leading to complexes with C-bound tetrazolate ligands, *i.e.*  $\{C(NNN^o)=N^bR(N^a-N^b)\}$ .<sup>9</sup> The mechanisms of these processes can be concerted or stepwise; in the latter case the formal CA is completely asynchronous and occurs via formation of an acyclic intermediate followed by ring-closure.



**Scheme 2.** Metal-mediated generation of tetrazolate species.

Inspection of literature relevant to metal-involving CA between azides and isocyanides<sup>14, 15</sup> indicated that up to now a substantial number of reports was devoted to reactions between *uncomplexed isocyanides* and metal-bound azides at palladium(II),<sup>16-26</sup> platinum(II),<sup>16, 19-21, 25, 27, 28</sup> gold(I),<sup>29</sup> gold(III),<sup>18, 30, 31</sup> and nickel(II)<sup>21, 32</sup> centers (**Scheme 2, route E**). In the vast majority of cases,<sup>17-20, 23-25, 27, 29, 32</sup> it is believed that CA proceeds through the attack of the free isocyanide on a complexed azide, albeit no mechanistic studies were undertaken. In one work,<sup>33</sup> it is suggested that the reaction starts from the joint coordination of azide and isocyanide to a metal center giving an intermediate pentacoordinated species that is subsequently transformed into C-tetrazolates via an intramolecular CA (**route H**). However, the latter mechanism was neither supported experimentally, nor theoretically.

An alternative approach to generation of tetrazolate complexes via CA is based on the use of *metal-bound isocyanides* and uncomplexed azide ion. Until now this approach was represented by a single study where CA was conducted at a platinum(II) center (**route F**) when the isocyanide complexes  $[Pt(PPh_3)_2(CNMe)_2][BF_4]_2$  and  $[Pt(diphos)(CNMe)_2][PF_6]_2$  were treated with one and two equivs  $NaN_3$  in water, correspondingly, and CA led to the C-tetrazolate species  $[Pt(PPh_3)_2(CNMe)(CN_4Me)][BF_4]$  (78%) and  $[Pt(diphos)(CN_4Me)_2]$  (90%), respectively.<sup>33</sup> As believed, this CA proceeds by attack of azide ion on the square-planar complex to give an intermediate five-coordinate species (**route H**), which then undergoes a facile cyclization accomplishing the tetrazolate complexes.

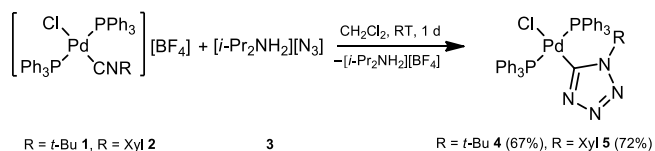
In principle, the mechanism of metal-mediated CA between isocyanides and azides could involve complexed azide as dipole and uncomplexed CNR as dipolarophile (Sustman III type of CA;<sup>34</sup> **route E**), metal-bound isocyanide as dipolarophile and free azide as dipole (Sustman I type of CA;<sup>34</sup> **route F**), and joint coordination of the reactants furnishing C-tetrazolate species (**route H**). Alternatively the reaction between metal-azides and isocyanides may proceed via the azide substitution step followed by CA (**routes G–F**).

In pursuit of our previous studies on CA to metal-bound (in particular to Pd<sup>II</sup>-ligated) nitriles (see our reviews,<sup>35</sup> recent experimental,<sup>36-39</sup> and also theoretical<sup>40-45</sup> works) and isocyanides

(see reviews<sup>9</sup>, experimental,<sup>13, 46</sup> and theoretical<sup>47-49</sup> works), we decided to verify the most probable route for generation of palladium(II)-tetrazolates from RNCs and  $N_3^-$ . To reach this goal we, first of all, decided to find experimental evidences that the palladium-tetrazolates could be obtained not only by the known reaction between (azide)Pd<sup>II</sup> species and uncomplexed RNCs<sup>16-26</sup>, but also via yet unreported integration of some (RNC)Pd<sup>II</sup> precursors and uncomplexed azide. These experimental examples should form the solid background for theoretical works directed toward verification of a plausible reaction mechanism that may proceed via routes **E, F, H, or G–F (Scheme 2)**, establishment of driving forces of the generation of (tetrazolate)Pd<sup>II</sup> complexes and identification of key intermediates of this palladium(II)-mediated integration.

## Results and Discussion

**Cycloaddition of Azide to Pd<sup>II</sup>-bound Isocyanides.** In order to verify the reactivity of palladium-isocyanide species toward  $N_3^-$ , we attempted to carry out CA of diisopropylammonium azide **3** to the isocyanide ligands in *trans*- $[PdCl(PPh_3)_2(CNR)][BF_4]$ <sup>50</sup> (R = *t*-Bu **1**, Xyl **2**). Reaction between equimolar amounts of complex **1** (or **2**) and **3** proceeds in  $CH_2Cl_2$  at room temperature (RT) for *ca.* 1 d giving the tetrazolate *trans*- $[PdCl(PPh_3)_2(CN_4t-Bu)]$  (**4**) or *trans*- $[PdCl(PPh_3)_2(CN_4Xyl)]$  (**5**) (**Scheme 3**) species. After evaporation of the solvent, these complexes were washed with MeOH/Et<sub>2</sub>O mixture (1:1, v/v) and purified by recrystallization from a  $CH_2Cl_2$ /Et<sub>2</sub>O mixture giving **4** (67%) and **5** (72%) in good isolated yields.

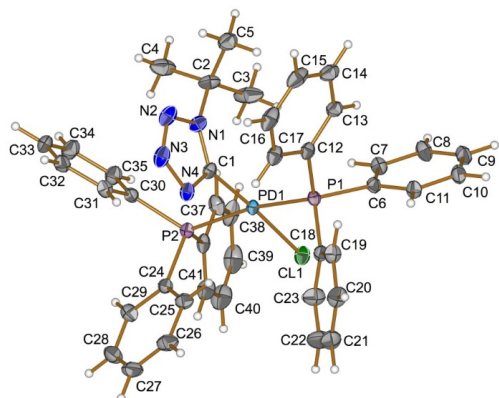


**Scheme 3.** Reaction between *trans*- $[PdCl(PPh_3)_2(CNR)][BF_4]$  (R = *t*-Bu **1**, Xyl **2**) and diisopropylammonium azide (**3**).

Complexes **4** and **5** were obtained as pale yellow solids and characterized by elemental analyses (C, H, N), HRESI<sup>+</sup>-MS, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies. In addition, the structure of **4** was elucidated by a single-crystal X-ray diffraction. Complexes **4** and **5** gave satisfactory C, H, and N elemental analyses, which are consistent with the proposed formulae. The ESI<sup>+</sup> mass spectra demonstrated a fragmentation pattern corresponding to the loss of Cl from the molecular ion along with the characteristic isotopic distribution. CA of **3** to **1** or **2** is accompanied by a pronounced downfield  $\delta^{13}C$  shift of the isocyanide quaternary C atom to the range common for tetrazolate ring Pd–CN<sub>4</sub>R ( $\delta_C$  150–165 ppm).<sup>16-21, 26, 27</sup> In **4** and **5**, the CN<sub>4</sub>R <sup>13</sup>C signals were found to resonate at  $\delta_C$  151.5 and 161.9 ppm, respectively; that is *ca.* 45 ppm downfield shifted vs. **1** and **2** (*e.g.* 115 ppm for C≡N in **1**).

In **4** (**Figure 1**), the PPh<sub>3</sub> are mutually *trans* (P1–Pd1–P2 167.93(2)°) and a slightly distorted square-planar environment around the metal center is completed with one tetrazolate and one chloride ligand. Bond angles around Pd as vertex are all within 3.0° of the values for an ideal square-plane. The Pd–C distance [Pd1–C1

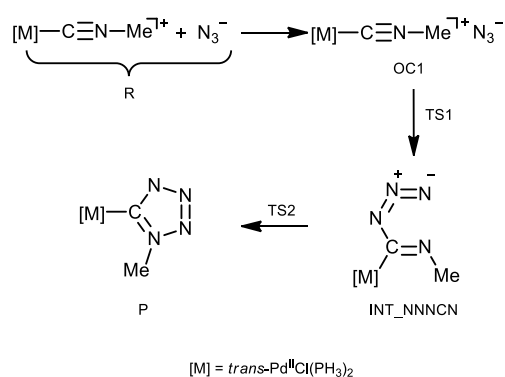
1.989(2) Å] is comparable to those reported for the related palladium tetrazolate complex *trans*-[Pd(PMe<sub>3</sub>)<sub>2</sub>(C<sub>4</sub>Xyl)(N=C=NR)] (2.006(5) Å).<sup>20</sup>



**Figure 1.** View of **4** with the atomic numbering schemes. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen labels are omitted for simplicity.

Our little synthetic experiment proved that the integration between RNC and N<sub>3</sub><sup>−</sup> species giving *C*-tetrazolate complexes might proceed via **route F** (**Scheme 2**) not only at platinum(II),<sup>33</sup> but also at palladium(II) centers. These data form the background for further theoretical study aimed toward verification of plausible mechanism of this reaction and results of the study are disclosed in the next section.

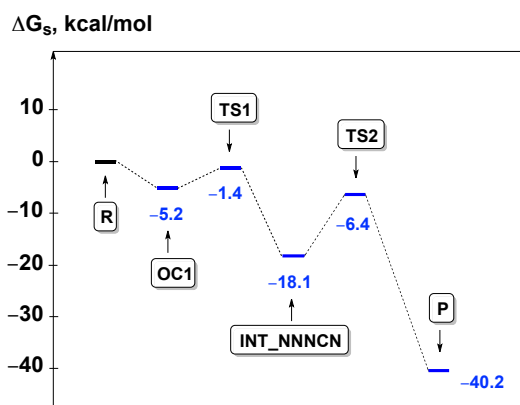
**Theoretical Study.** In order to shed light on the mechanism of the Pd<sup>II</sup>-mediated azide–isocyanide integration, a quantum chemical DFT study of this process in a model system was undertaken (CPCM-B3LYP/6-311+G(d,p)//gas-B3LYP/6-31G(d)). The route **F** was found the most preferred out of all possible reaction paths shown in **Scheme 2**. Discussion about this and other plausible reaction channels is given below.



**Scheme 4.** Mechanism of Pd<sup>II</sup>-mediated azide–isocyanide integration.

The mechanism of the formation of (tetrazolate)Pd<sup>II</sup> complexes via formal CA of N<sub>3</sub><sup>−</sup> to *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(CNMe)]<sup>+</sup> complexes (**Scheme 2, route F**) was found to be stepwise (**Scheme 4**).

The process is initiated by the formation of the orientation complex *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(CNMe)]<sup>+</sup>•N<sub>3</sub><sup>−</sup> (**OC1**), and two transition states (TSs) were located. The first one (**TS1**) corresponds to the formation of the C–N bond giving the acyclic NNNCN-intermediate (**INT\_NNNCN**) and the second one (**TS2**) is associated with the ring closure forming the *C*-tetrazolate complex *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(C<sub>4</sub>Me)] (**P**). The second step is the rate limiting (**Figure 2, Table S3**). Noteworthy that we were unable to locate on the potential energy surface any TSs for the concerted pathway or other acyclic NNNCN-intermediates. Based upon our quantum chemical calculations one can state that the formation of the *C*-tetrazolate palladium complexes *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(C<sub>4</sub>Me)] from coordinated isocyanides and free azides is quite favorable from both kinetic and thermodynamic viewpoints.



**Figure 2.** Energy profile of **R** → **P** transformation for Pd<sup>II</sup>-mediated azide–isocyanide integration.

We estimated the relative stability of two possible types of the orientation complexes in the model reaction system, *viz.* *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(CNMe)]<sup>+</sup>•N<sub>3</sub><sup>−</sup> (**OC1**) versus *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)]•CNMe (**OC2**) and found that the **OC1** → **OC2** transformation (**Scheme 2, inverse route G**) is just slightly thermodynamically favorable (ΔG<sub>s</sub> = −1.0 kcal/mol). Taking this into account, the hypothetical reactions between uncomplexed isocyanide and metal-bound azide (**Scheme 2, route E**) were also inspected (**Table S3**) and the following conclusions can be drawn. Firstly, we were unable to locate any TSs and intermediates for the CNMe + *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)] → *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(C<sub>4</sub>Me)] processes. Secondly, we found two TSs (**TS3** and **TS4**) for the CNMe + *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)] → N<sub>2</sub> + *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(N=C=NMe)] (ΔG<sub>s</sub><sup>‡</sup> = 36.2 kcal/mol, ΔG<sub>s</sub> = −62.2 kcal/mol) and CNMe + *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)] → *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(N<sub>2</sub>)]<sup>+</sup> + N=C=NMe<sup>−</sup> (ΔG<sub>s</sub><sup>‡</sup> = 39.0 kcal/mol, ΔG<sub>s</sub> = −9.0 kcal/mol) concerted transformations. Obviously that although being thermodynamically favorable these paths are not realized at room temperature due to too high activation barriers.

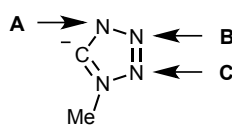
In order to verify the hypothesis<sup>33</sup> on formation of intermediates bearing both azide and isocyanide species bound to the metal center (**Scheme 2, route H**), we undertook an extensive search of appropriate minima on the potential energy surface with various mutual positions of these ligands in the model starting structures. However, we were unable to locate any pentacoordinated intermediates, and all attempts to fix them led to the migration of one ligand from the coordination sphere of the

metal center during the geometry optimization procedure or to the collapse of the whole structure of the palladium model complex. Hence, **route H** can be excluded from consideration.

The metal-free reaction  $\text{N}_3^- + \text{CNMe} \rightarrow \text{CN}_4\text{Me}^-$  is thermodynamically unfavorable ( $\Delta G_s = 4.7$  kcal/mol) and we were unable to locate appropriate TSs and intermediates for both concerted and stepwise paths. However, we found TS (**TS<sub>metal-free</sub>**) for the  $\text{N}_3^- + \text{CNMe} \rightarrow \text{N}_2 + \text{N}=\text{C}=\text{NMe}^-$  concerted transformation and it is highly thermodynamically favorable ( $\Delta G_s = -55.5$  kcal/mol), but kinetically hindered ( $\Delta G_s^\ddagger = 35.2$  kcal/mol).

We checked the tendency toward decomposition of *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(CN<sub>4</sub>Me)] complexes and uncomplexed tetrazolate CN<sub>4</sub>Me<sup>−</sup> via the paths *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(CN<sub>4</sub>Me)]  $\rightarrow$  N<sub>2</sub> + *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(N=C=NMe)] (by **TS5**) and CN<sub>4</sub>Me<sup>−</sup>  $\rightarrow$  N<sub>2</sub> + N=C=NMe<sup>−</sup> (by **TS5<sub>metal-free</sub>**), respectively (**Table S3**). One can conclude that the tetrazolate CN<sub>4</sub>Me<sup>−</sup> species are very susceptible to decomposition ( $\Delta G_s^\ddagger = 10.8$  kcal/mol,  $\Delta G_s = -60.2$  kcal/mol), but the palladium center is excellent stabilizer for such anionic species ( $\Delta G_s^\ddagger = 36.5$  kcal/mol,  $\Delta G_s = -35.2$  kcal/mol).

Finally, we compared the thermodynamic stability of the tetrazolate complexes *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(CN<sub>4</sub>Me)], where the CN<sub>4</sub>Me<sup>−</sup> ligand is coordinated to the metal by different alternative sites (**Figure 3**). The stability series is the following: *trans*-[PdCl(PH<sub>3</sub>)<sub>2</sub>(CN<sub>4</sub>Me)] (0 kcal/mol in terms of Gibbs free energy in solution, internal standard) > **A** (24.4 kcal/mol) > **B** (33.9 kcal/mol) > **C** (42.2 kcal/mol).



**Figure 3.** Alternative binding sites of the tetrazolate ligand.

## Experimental Section

**Materials and Instrumentation.** Solvents and reagents were obtained from commercial sources and used as received, apart from chloroform, which was purified by the conventional distillation over calcium chloride. Complexes **1–2** were prepared by the known procedures.<sup>50</sup> C, H, and N elemental analyses were carried out on a Euro EA 3028HT CHNSO analyzer. Mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source and MeCN was used as the solvents. The instrument was operated both at positive and negative ion modes using *m/z* range of 50–3000. The capillary voltage of the ion source was set at −4500 V (ESI<sup>+</sup>) or 3500 V (ESI<sup>−</sup>) and the capillary exit at  $\pm(70\text{--}150)$  V. The nebulizer gas pressure was 0.4 bar and drying gas flow 4.0 L/min. The most intensive peak in the isotopic pattern is reported. Infrared spectra (4000–400 cm<sup>−1</sup>) were recorded on a Shimadzu FTIR 8400S instrument in KBr pellets. 1D (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, DEPT) NMR spectra were acquired on a Bruker Avance 400 spectrometer at ambient temperature.

### Synthetic Work

**Cycloaddition of 3 to [PdCl(PPh<sub>3</sub>)<sub>2</sub>(CNR)][BF<sub>4</sub>].** A solution of **3** (22 mg, 0.15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added to a solution of **1** or **2** (0.15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) and the reaction mixture was stirred at RT. After 1d, the solvent was evaporated at RT, the residue was

washed with a Et<sub>2</sub>O (6 mL) and MeOH (1 mL) mixture. The products were slowly recrystallized from a CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O (1:1, v/v) mixture at RT.

**4** (80 mg, 67%). Anal. Calcd. for C<sub>41</sub>H<sub>39</sub>N<sub>4</sub>ClP<sub>2</sub>Pd: C, 61.21; H, 4.97; N, 7.08. Found: C, 61.44; H, 4.98; N, 7.12. HRESI<sup>+</sup>-MS, *m/z*: calcd. for C<sub>41</sub>H<sub>39</sub>N<sub>4</sub>P<sub>2</sub>Pd<sup>+</sup> 755.1679, found 755.1652 [M − Cl]<sup>+</sup>. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.21 (s, 9H, CH<sub>3</sub>), 7.32 (t, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 12H), 7.40 (t, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 6H), 7.47 (q, <sup>3</sup>J<sub>H,H</sub> = 6.2 Hz, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, CDCl<sub>3</sub>,  $\delta$ ): 30.2 (CH<sub>3</sub>), 58.0 (C(CH<sub>3</sub>)<sub>3</sub>), 128.4 (t, J<sub>C,P</sub> = 5 Hz, CH, C from PPh<sub>3</sub>), 129.8 (t, J<sub>C,P</sub> = 24 Hz, C, C from PPh<sub>3</sub>), 130.6 (CH, C from PPh<sub>3</sub>), 134.5 (t, J<sub>C,P</sub> = 6 Hz, CH, C from PPh<sub>3</sub>), 151.5 (C, C from the tetrazolate ring).

**5** (88 mg, 72%). Anal. Calcd. for C<sub>45</sub>H<sub>39</sub>N<sub>4</sub>ClP<sub>2</sub>Pd: C, 64.37; H, 4.68; N, 6.67. Found: C, 63.42; H, 4.64; N, 6.70. HRESI<sup>+</sup>-MS, *m/z*: calcd. for C<sub>45</sub>H<sub>39</sub>N<sub>4</sub>P<sub>2</sub>Pd<sup>+</sup> 803.1679, found 803.1661 [M − Cl]<sup>+</sup>. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>,  $\delta$ ): 2.22 (s, 6H, CH<sub>3</sub>), 6.96 (d, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 12H), 7.12–7.72 (m, 32H). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, CDCl<sub>3</sub>,  $\delta$ ): 21.0 (CH<sub>3</sub>), 128.0–136.2 (C from Xyl and PPh<sub>3</sub>), 161.9 (C, C from the tetrazolate ring).

### X-ray Structure Determination

The crystal of **4** was immersed in cryo-oil, mounted in a MiTeGen loop, and measured at a temperature of 123 K. The X-ray diffraction data was collected on a Bruker Axs KappaCCD diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The Denzo-Scalepack<sup>51</sup> program package was used for cell refinement and data reduction. The structure was solved by charge flipping method using Superflip<sup>52</sup> program with the Olex2<sup>53</sup> graphical user interface. A semi-empirical absorption correction (SADABS)<sup>54</sup> was applied to the data. Structural refinement was carried out using SHELXL-97.<sup>55</sup> Hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95–1.00 and U<sub>iso</sub> = 1.2–1.5 U<sub>eq</sub>(parent atom). The crystallographic details are summarized in **Table S1** (see ESI). CCDC-1414621 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Computational Details

The full geometry optimization of all structures and transition states was carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang and Parr (B3LYP)<sup>56, 57</sup> with the help of the Gaussian-09<sup>58</sup> program package. No symmetry operations have been applied. The geometry optimization was carried out using a quasi-relativistic Stuttgart pseudopotential that described 28 core electrons and the appropriate contracted basis sets<sup>59</sup> for the palladium atoms and the 6-31G(d) basis set for other atoms. Single-point calculations were performed on the basis of the equilibrium geometries found by using the 6-311+G(d,p) basis set for nonmetal atoms. As was shown previously,<sup>40, 41, 43–45</sup> this approach is sufficiently accurate for the description of CAs to the C=N triple bond providing results close to those obtained by such methods as MP2, MP4, CCSD(T), CBS-Q, and G3B3.

The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima (no imaginary frequencies) or saddle points (only one imaginary frequency), and to estimate the thermodynamic parameters, the latter being calculated at 25 °C. The nature of all transition states was investigated by the analysis of vectors associated with the

imaginary frequency and by the calculations of the intrinsic reaction coordinates (IRC) using the Gonzalez–Schlegel method.<sup>60–62</sup>

The total energies corrected for solvent effects ( $E_s$ ) were estimated at the single-point calculations on the basis of gas-phase geometries at the CPCM-B3LYP/6-311+G(d,p)//gas-B3LYP/6-31G(d) level of theory using the polarizable continuum model in the CPCM version<sup>63,64</sup> with  $\text{CH}_2\text{Cl}_2$  as solvent. The UAKS model was applied for the molecular cavity and dispersion, cavitation, and repulsion terms were taken into account. The entropic term in  $\text{CH}_2\text{Cl}_2$  solution ( $S_s$ ) was calculated according to the procedure described by Wertz<sup>65</sup> and Cooper and Ziegler<sup>66</sup> (see eqs. 1–4), as well as enthalpies and Gibbs free energies in solution ( $H_s$  and  $G_s$ ) using the expressions 5 and 6 (all equations are provided in Supplementary information)

## Conclusions

The results of this work could be considered from the following perspectives. Firstly, in pursuit of our studies on CA to metal-bound RNCs,<sup>13, 46–49</sup> we observed that the metal-mediated reaction between equimolar amounts of the isocyanide ligand in *trans*- $[\text{PdCl}(\text{PPh}_3)_2(\text{CNR})][\text{BF}_4]$  ( $R = t\text{-Bu, Xyl}$ ) and diisopropylammonium azide proceeds in  $\text{CDCl}_3$  at RT furnishing the *C*-tetrazolate complexes *trans*- $[\text{PdCl}(\text{PPh}_3)_2(\text{CN}_4\text{R})]$  (ca. 70%). Generation of *C*-tetrazolato ligands from metal-bound RNCs and uncomplexed  $\text{N}_3^-$  was previously observed only at a platinum(II) center, whereas many other synthetic routes to *C*-tetrazolato metal complexes involve reaction between metal-bound azide and uncomplexed isocyanides.

Secondly, based upon quantum chemical calculations we established that the mechanism for the formal CA of  $\text{N}_3^-$  to *trans*- $[\text{PdCl}(\text{PPh}_3)_2(\text{CNMe})]^+$  is stepwise. The process is both kinetically and thermodynamically favorable and occurs via the formation of the acyclic NNNCN-intermediate. The second step of formal CA, *i.e.* cyclization, is the rate limiting. Despite the fact that the substitution of CNMe by  $\text{N}_3^-$  ligand is slightly thermodynamically favorable, we were unable to find the paths on the potential energy surface for the hypothetical CA between uncomplexed isocyanide and palladium-bound azide. Thus, we believe that the experimentally observed palladium tetrazolate complexes is, in fact, generated from the negatively charged uncomplexed azide and positively charged metal-bound isocyanide species, and this reaction path is favorable from the viewpoint of Coulomb attraction. However, the alternative mechanism that involves complexed azide and uncomplexed RNCs (**Scheme 2, route E**) can be feasible at other metal centers and the previously obtained synthetic results collaterally confirm this assumption. Hence, the previous works<sup>16–26</sup> should be thoroughly revisited and the possibility of the alternative reaction path should be verified by theoretical calculations thus giving a general picture of this synthetically useful metal-mediated integration.

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